ISOSTRUCTURAL HKUST-1 METAL-ORGANIC FRAMEWORKS AS CATALYSTS FOR LIQUID-PHASE OXIDATION OF HYDROCARBONS

BY

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Dedication

To my parents for their support and understanding.

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All thanks and adoration to Almighty Allah for making the successful completion of my MS degree program a reality. My unfeigned appreciations go to my thesis advisor, Dr. Abdul Malik Peedikakkal for his thoughtful, proper coordination and supervision of the entire work. My profound gratitude also goes to my thesis committee members, Dr. Bassam El Ali and Dr. Nasiruzamman Shaikh for their support, review of the thesis report and important recommendations. I also thank the Centre of Excellence in Nanotechnology (CENT)director, Dr. ZainHassan Abdallah Yamanifor allowing me to undertake my work in the Centre, using the CENT instruments and laboratory and for providing other logistic supports. I must also express special thanks to Dr. Aasif Helal of CENT for his support throughout the thesis research work. The efforts of the following are also appreciated for helping me with various analysis, Dr. Abbas Saeed Hakeem (SEM and XRD),Mr.Irshad Baig (ICP-MS), Mr. Muhammad Qamarrudin (GC-MS and GC-FID). On the final note, I acknowledge the support of the department of chemistry through the chairman, Dr. AbdulAziz Al-Saadi most especially for providing some instrument sused during this research and KFUPM for offering me studentship for my MS study

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ABSTRACT

Full Name : Jimoh Abiola Azeez

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The increasing demand for safer and energy-saving reaction routes resulted in the need to develop new materials which are highly tunable and reusable for small and large scale chemical processes. Hence, catalyst development is an ever-growing area of research. In recent times, chemists have endorsed MOFs as viable catalysts to route the course of new and existing chemical reactions, to reduce industrial wastes and enable greener chemical processes. The great potential of MOFs for catalysis is due to their tunability, high surface area and variable stability. This work is focused on the solvothermal synthesis of some isostructural HKUST-1 metal-organic frameworks using well known solvothermal methods followed by modification of the synthesized Zn-HKUST MOFs with the aid of post-synthetic metallic exchange. The obtained MOFs were characterized using Powder X-ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The catalysts were further applied for the oxidation of toluene, cyclohexane and methylcyclohexane using methods reported in the literature. GC-MS and GC-FID analysis revealed that Fe-Zn-HKUST-1 shows the best activity in terms of benzaldehyde selectivity for the oxidation of toluene. However, HKUST-1 gave the highest conversion of 52% for cyclohexane and methylcyclohexane oxidation.

ملخص الرسالة

الاسم الكامل:جيمو أبيولا العزيز

عنوان الرسالة:HKUST-1 المعادن العضوية أطر كحافز لل أكسدة السائل مرحلة من المحروقات

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لقد أدى الطلب المتزايد على التفاعلات الآمنة الموفرة للطاقة إلى العمل على تطوير مواد جديدة يمكن التحكم فيها و إعادة استخدامها مرة أخرى فى العمليات الكيميائية على المستوى المعملى والصناعى;و من ثم أصبح تطوير العوامل الحفازة أحد الموضوعات البحثية الأكثر نموا هذه الأيام.

قام العلماء مؤخرا" بتصنيع MOFs، و هى عبارة عن مواد فى شكل شبكة أو إطار من مادة عضوية تحوى بداخلها ذرات لفلز, كعامل حفاز حيوى لتنشيط عدد من التفاعلات المعروفة و المستحدثة للحد من المخلفات الصناعية و تدعيم العمليات الكيميائية الغير مضرة بالبيئة. و تتميز هذه المركبات بأنها يمكن تغيير تركيبها الكيميائى بسهولة, هذا بالإضافة إلى تمتعها بمساحة سطح عالية و ثبات غير متناهى.

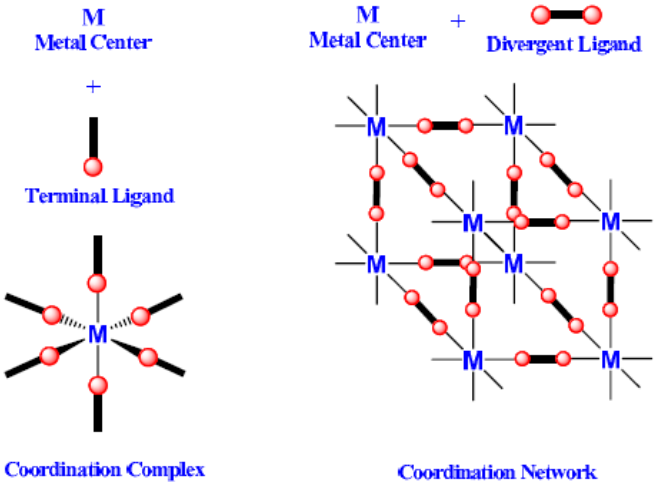
لقد قمنا فى هذا البحث بتحضير HKUST-1 MOFs عن طريق solvothermal synthesis و من ثم تعديلها عن طريق تبادل الأيونات بعد تحضيرها, ثم توصيفها باستخدام PXRD و FTIR و FESEM و ICP-MS و من ثم استخدامها فى أكسدة الطولوين, الهكسان الحلقى, و ميثيل الهكسان الحلقى باستخدام طرق كيميائية معروفة.

; يتمتع بأعلى فاعلية لأكسدة الطولوين إلىبنزالدهد-Fe-Zn-HKUST أن GC-FID و GC-MSلقد أثبتت التحاليل باستخدام أدى إلى أكسدة 52% من الهكسان الحلقى و ميثيل الهكسان الحلقى HKUST-1إلا أن استخدام

CHAPTER 1

INTRODUCTION

Metal - Organic Frameworks (MOFs) are crystalline, highly porous coordination polymers which comprise of inorganic units (metal) coordinated to rigid organic fragments. They were first built by a node-linker approach that was first described by Robson [1]. This method uses metal ions as nodes and organic ligands as linkers. In this case, a metal ion with a preferred coordination number and geometry combines with divergent ligand molecules to form an extended 1D, 2D or 3D networks. The metal-linker interactions vary widely and have included ion-ion interactions, ion-dipole, dipole-dipole, hydrogen bonding, anion- π interactions, π - π interactions [2] as well as van-der Waals interactions [3]. The strength of these interactions has been proven to directly influence the overall stability of the resulting framework [4]. Extended networks can be developed from the basic principles guiding the formation of coordination complexes **(Figure 1**). Hence, the choice of metal center affects the resulting framework structure because a given metal has preference for specific geometry and coordination environment.



coordination polymers.

A second approach to the synthesis of MOFs was described by Yaghi [5, 6]. This involves the use of multitopic organic ligands as linker and metal ions or clusters (secondary building units, SBUs) as nodes. This method enables unprecedented network extension with retention of the core structure of the linker (**Figure 2**).

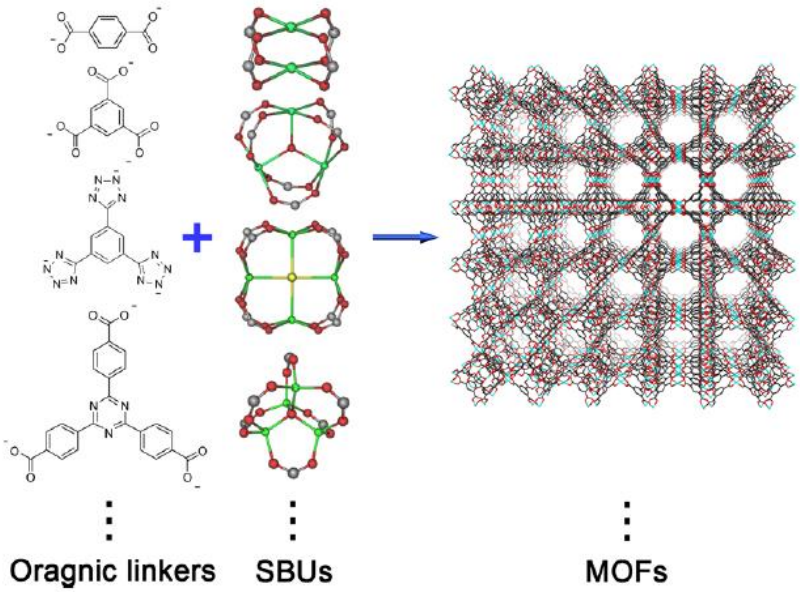


Figure 3: Illustration of MOF synthesis and structure.

Most often, MOFs are easily synthesized by means of hydrothermal or solvothermal [7-11] which involve high temperature self-assembly in a high boiling organic solvent or water in closed vessels. However, these methods typically require long reaction times, from several hours up to

several days, depending upon the nature of ligand, the reaction solvent, reagent concentrations and reaction temperature. They can also be produced using the microwave assisted process which allows the large scale synthesis of MOFs in a few minutes [12-14].

MOF-5 is one of the first series of MOFs to be reported and fully characterized. It consists of an octahedral secondary building unit (SBU) which is made from Zn_4O $(CO_2)_6$ as inorganic unit which comprises of four ZnO_4 tetrahedra with a common vertex and six carboxylate groups. These octahedral SBUs are joined together by benzene linkers [15]. These unique units lead to a perfect cubic network whose vertices comprises of the SBUs and the edges are made up of the benzene links (**Figure 3**). This compound was synthesized from Zn(II) and 1,4-benzenedicarboxylic acid (BDC) under organic conditions pre-determined to form the SBU *in situ*. Since the benzene links and the SBUs appear to be relatively rigid and large entities, resulting structure has exceptionally high porosity (indicated by its sorption), and stability [16]

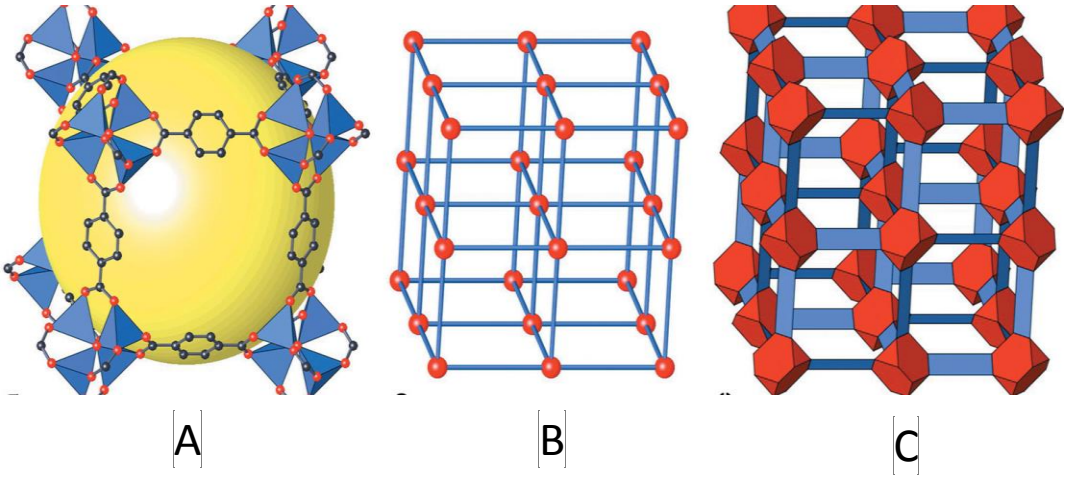


Figure 3: **A)** The structure of MOF-5 represented as ZnO_4 tetrahedra (blue shapes) linked by benzene dicarboxylate linkers to form an extended 3D cubic framework with interconnected pores of 8 Å aperture width and 12 Å pore (yellow ball) diameter. **B)** The topology of the MOF structure shown as a ball-and-stick model. **C)** The structure represented $(OZn_4)O_{12}$ cluster (red tetrahedron) and BDC ions (blue connection). The opposing lines are all at exactly 90°.

MOFs have been found to possess unique properties like high surface areas (up to 10400 m^2/g) [17] and tunable pores that can be used in various potential applications such as gas storage [18]catalysis [19], separation [20] and drug delivery [21]. They have also been found to be candidates for other applications like microelectronics [22], sensing [23], optics [24], micro-motors [25], molecular rotors [26],and bioreactors [27]. Presently, the most highly recognized applications of MOFs, however, has been in the areas of gas storage and separation. The strong interests in this research area promote the urgent need to develop viable technologies for hydrogen fuel storage for commercial use as well as to control the concentration CO_2 in the atmosphere.

High surface area and possibility of structural modification amongst other desirable physical and chemical properties make it possible for MOFs to efficiently catalyze broad range of reactions [19]. They are usually modified by a method that is broadly known as Post-Synthetic Modification (PSM). PSM makes it possible to incorporate a highly diverse range of different functional groups making it free of the restrictions resulting from the synthetic conditions of the MOFs. It also allows introduction of multiple metal ions into a single framework in a combinatorial manner, enabling an effective way to systematically fine-tune and optimize MOF properties [28]. The process in which new metal sites are incorporated into a MOF framework is known as transmetallation or post-synthetic metal exchange and the MOFs produced by this method can be described as isostructural MOFs with similar structural frameworks but different metal ions (**Figure 4**).

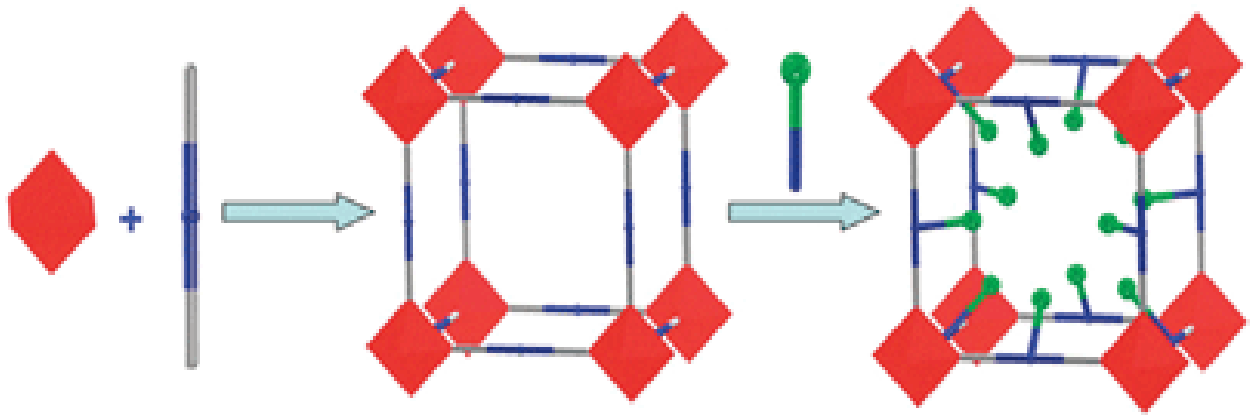


Figure 4: A general scheme for the post-synthetic modification of MOFs

This synthetic method can be used to obtain certain MOFs that cannot be obtained via conventional synthetic methods. Cation exchange also helps to enhance the properties of some MOFs by making it possible to incorporate a more useful metal site thereby improving some of their physical and chemical properties hence giving them more interesting applications. For example HKUST-1 has a surface area of about 1500 m^2/g and it contains Cu^{2+} but the iso-structure can be made by simply substituting the Cu^{2+} with other metals. A unique property of transmetallation lies in the fact that new MOFs can be obtained by complete or partial substitution of metal ions within the framework without altering the morphology of the MOFs (**Figure 5**). This process serves as an alternative, typically milder route for accessing new MOFs when conventional synthesis at high temperature fails [29]. This substitution occurs at the metal nodes, often called the inorganic clusters or secondary-building units (SBUs). Although the metal ions are integral parts of the MOFs structure, they can be replaced either completely or partially within hours or days without necessarily affecting the MOFs structure [30]. Transmetallation changes the properties of MOFs and also makes them useful for other important applications especially in

catalysis. The transmetallated MOFs has multiple properties having separate metal sites that can be utilized for specific catalytic conversion of the organic molecules.

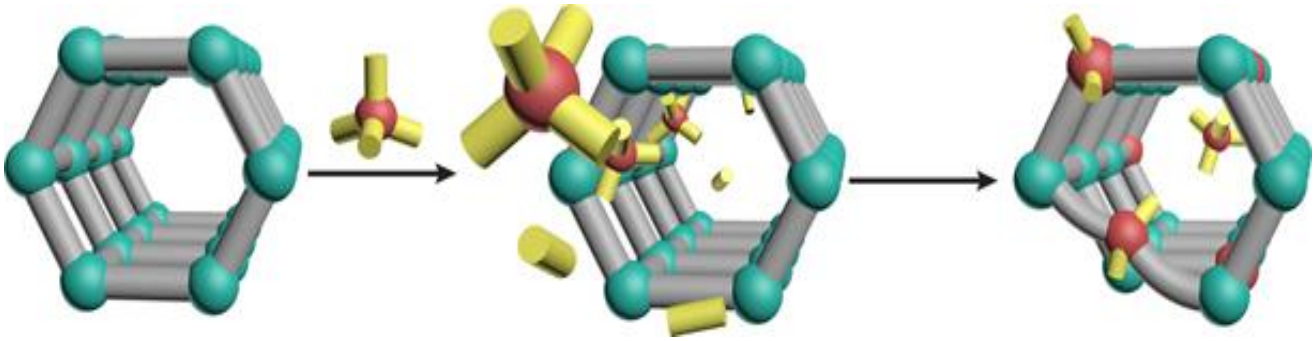


Figure 5: Schematic diagram for post synthetic metal exchange or transmetallation

The development of efficient new catalysts is still a serious challenge in chemical research. Hence the increasing demand for safer and energy-saving reaction routes stems out of the need to develop new materials and the global aim of combating serious environmental challenges that stem out of several industrial processes. Hence, catalyst development is an ever-growing area of research. In recent times, chemists have endorsed MOFs as viable heterogeneous catalysts to channel the course of new and existing chemical reactions, to reduce industrial wastes and enable greener chemical processes. This quest embarked upon by chemists will facilitate better understanding of physical and chemical processes like surface interactions, reaction mechanisms and also pave a new way for novel concepts and ideas for the next generation of curious minds. The role of heterogeneous catalysts either in chemical or petrochemical industries cannot be overemphasized. They reduce the enormous wastes that are associated with homogeneous catalysts and also reduce cost due to their reusability. They occur in different phase from the

substrates and usually work based on adsorption mechanism. They are mostly solids on which liquid or gaseous reaction mixtures are adsorbed. The active site may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two. Thus, not only most of the volume, but also most of the surface of a heterogeneous catalyst may be catalytically inactive. The dependence of catalytic activity of surface area, pore volume makes MOFs catalysis a viable area of chemical research. Finding out the nature of the active site requires technically challenging research. Thus, research for finding out new metal and ligand combinations for catalysis continues.

These highly porous, crystalline MOFs have some of the catalytically important properties of zeolites like uniform cavity and pore sizes as well as medium to large internal surface areas[31]. Unlike zeolites, vast chemical varieties of MOFs can be synthesized due to the presence of infinite organic linkers. This suggests that the catalytic niche of MOFs is likely be high-valueadded reactions such as production of specific enantiomers, sensitive molecules as well as production of fine chemicals, which require specific and tunable catalytic sites [32].Despite the various interesting and compelling recent developments in MOFs catalysis, the area of MOFs catalysis is still in an immature phase.Many researchers have likened MOFs catalysis to enzyme catalysis, they look forward to the development of the catalytic chemistry in the direction of an ‘‘artificial enzyme’’. On the overall, the uniqueness of MOFs over other materials is yet to be fully illustrated since they have not been reported to be of use in the chemical or petrochemical industries.

Oxidation reactions among the most important chemical conversions in industries and laboratories. Conversion of abundant and cheap hydrocarbons like toluene, cycloalkanes and methylcyclohexane into more valuable chemicals like aldehydes, ketones and acids stands as a

significant process for consideration [33]. Among the useful transformations, the direct oxidation of toluene to produce benzaldehyde is an attractive process. Toluene oxidation gives a mixture of oxygenated products like benzoic acid, benzyl alcohol, benzaldehyde and cresols. Commercially, benzaldehyde is mainly produced by the chlorination of toluene followed by the hydrolysis process, which generates large amounts of toxic acidic/basic discard solution, leading to equipment corrosion and environmental pollution. Even worse, the benzaldehyde produced by this route is not qualified to synthesize some high-quality compounds such as perfumes or pharmaceuticals because the product contains chlorine [34]. Therefore, there is a clear need to develop new materials to fast-track the selective oxidation of toluene as an alternative route to produce benzaldehyde and consequently benzoic acid.

Alkanes are naturally abundant and cheap carbon-containing raw materials which serve as attractive substrates for production of value-added organic chemicals (alcohols, ketones, aldehydes and carboxylic acids) [35]. Unfortunately, the chemical inertness of these compounds is a considerable limitation towards their vast application for direct syntheses of oxygenated products under relatively mild conditions. However, a good choice of metal catalyst and an appropriate oxidizing agent, as well as properly controlled reaction conditions, can pave a way for a cleaner and efficient chemical industry. Today, over a billion tonnes of cyclohexanone and cyclohexanol are produced every year and they are mostly used for the synthesis of Mylon-6, 6 and Nylon-6 [36].

CHAPTER 2

LITERATURE REVIEW

Chui and coworkers were the first to synthesize HKUST-1 at the Hong Kong University of Science and Technology [11]. HKUST-1 was discovered to be a highly porous metal-coordination polymer $[Cu_3(BTC)_2(H_2O)_3]_n$(where BTC is benzene-1,3,5-tricarboxylate) which has interconnected $[Cu_2(O_2CR)_4]$ units, $C_{18}H_{12}O_{15}Cu_3$, (where R is an aromatic ring). It creates a 3-dimensional system of channels with a pore size of 1 nm and an accessible porosity of about 40 % in the solid. The single-crystal structural analysis of HKUST-1revealed that the polymer framework is composed of dimeric cupric tetracarboxylate building units (**Figure 6**), with a Cu-Cu inter-nuclear separation of 2.628(2) Å. The framework was found to be electrically neutral because the twelve carboxylate oxygens from the two BTC ligands bind to four coordination sites for each of the three Cu^{2+} ions of the formula unit [11]. Hence each Cu atom completes its pseudo-octahedral coordination sphere with the presence of axial aqua ligands opposite to the Cu-Cu dimer. The tetracarboxylate unit provides a structural motif with potential four-fold symmetry, and the trimesic acid provides a threefold symmetry element (**Figure 7**). The origin of the nano-channels can be clearly considered to arise from the formation of larger octahedral secondary building units (SBUs). The main SBU in HKUST-1 is the octahedral unit (**Figure 8, 9**) with Cu_2 at its 6 vertices and 4 trimesate ions tetrahedrally disposed as “panels” for four of the eight triangular faces of the octahedron.

The Zn-HKUST-1 that contains Zn^{2+} ions is analogous to HKUST-1 [12]. Analysis of Zn-HKUST-1 by powder X-ray diffraction and gas sorption shows the retention of crystalline

structure but negligible nitrogen uptake at 77 K due to a dense surface layer that prevents the passage of small molecular species into the crystal framework [56]. The prevalence of zinc paddlewheels in a variety of MOFs such as previously discusses HKUST-1 suggests that Zn is a promising metal with which an isostructural analogue to Cu-HKUST-1 can be constructed.

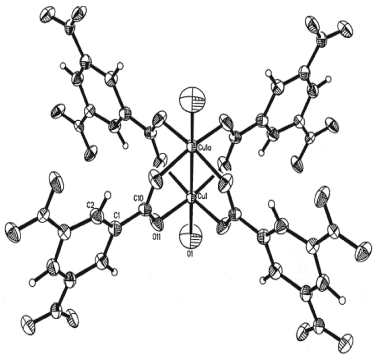


Figure 6: Dicopper(II) tetracarboxylate building block containing two axial aqua ligands

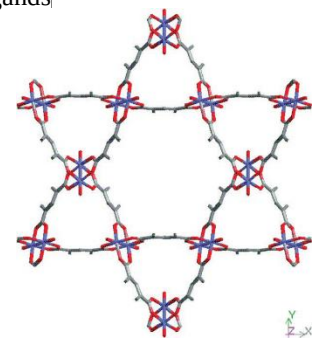


Figure 8:[Cu_3 $(TMA)_2(H_2O)_3$] viewed along thecell body diagonal, showing a hexagonal-*n*shaped window at the intersection of the nanopores.

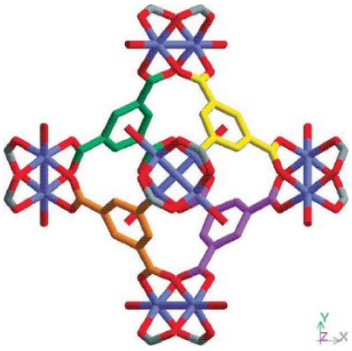


Figure 7: Secondary building unit (SBU) showing the tbo net topology and the paddlewheel structure

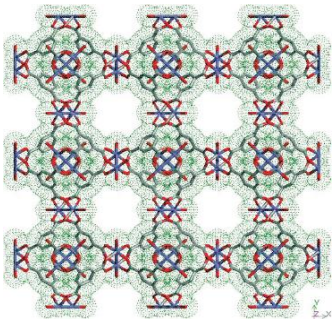


Figure 9: Polymer framework nanochannels with fourfold symmetry

2.1 Metal-Organic Frameworks as Catalyst

Over the past few decades, transition metal complexes comprising mainly of phosphine ligands, salen or salophen ligands, pincer ligands and N-heterocyclic carbenes (NHC) have made remarkable impact on catalysis. Worthy of mention are the Nobel-prize winning Noyori asymmetric hydrogenation [37], Sharpless oxidations (Sharpless epoxidation [38],Sharpless asymmetric dihydroxylation[39]and Sharpless oxyamination[40]) as well as Jacobsen epoxidation [41]. Most of these metal complexes have only been successful as homogeneous catalysts which have significant disadvantages like difficulty of product separation, poor reusability and toxicity.

Relatively insoluble and stable materials like zeolites, metals and metal oxides are widely used as heterogeneous catalysts on the industrial scale. Notable conversions like the Harber-Bosch, Contact process, Ostwald process, steam reforming, petrochemical reactions and Ziegler Natta polymerization make use of these insoluble materials. In terms of easy post-reaction separation, these materials have recorded huge success. There is still an urgent need to develop materials that will be more energy efficient, tunable, and more eco-friendly.

MOFs have shown great catalytic prospects for a wide range of reactions due to the diversity in their structures, low toxicity, reusability and cost effectiveness [7]. In fact, MOFs are among the best candidates in bridging the gap between homogeneous and heterogeneous catalysis. The metals in the MOF structure often act as Lewis acids especially when the frameworks are activated by removing the coordinated labile solvent molecules or counter ions [42].

Fujita *et al.* first reported the catalytic activity of a 2D Cd (II) - based MOF for the cyanosilylation of aldehydes. They obtained the unsaturated metal cluster by removing two water molecules from the octahedral structure of $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2].(NO_3)_2.4H_2O\}$ [43]. Fe(BTC) has also been used as

heterogeneous catalyst for the selective methylation of primary aromatic amines using dimethyl carbonate[44],efficient oxidation of benzylic compounds using t-butylhydroperoxide as oxidizing agent [45], and oxidation of thiols to disulfides [46].

Seo *et al.* first reported asymmetric catalysis using a homochiral MOF, $[Zn_3(\mu_3\text{-}O)(1\text{-}H)_6].2H_3O.12H_2O]$ for trans-esterification reaction. It was also the first MOF demonstrating that the organic linker embedded into a pore can catalyze an asymmetric reaction [47]. Lin *et al.*also reported the activity of a homochiral non-interpenetrating MOF which was constructed infinite 1-dimensional $[Cd(\mu\text{-}Cl)_2]_n$ zigzag chains with axial bipyridine bridging ligands containing orthogonal secondary functional groups[48]. The chiral secondary functional groups were used to generate a heterogeneous asymmetric catalyst for the addition of diethyl zinc to aromatic aldehydes to afford chiral secondary alcohols at up to 93% enantimeric excess (ee).

2.2 Catalytic Activity of HKUST-1

HKUST-1 has been particularly well recognized for its high catalytic activity especially when the axial aqua ligands are removed *via* activation (**Figure 10**). Activation gives unsaturated metal sites without affecting the rigid framework of the MOF [49, 50].

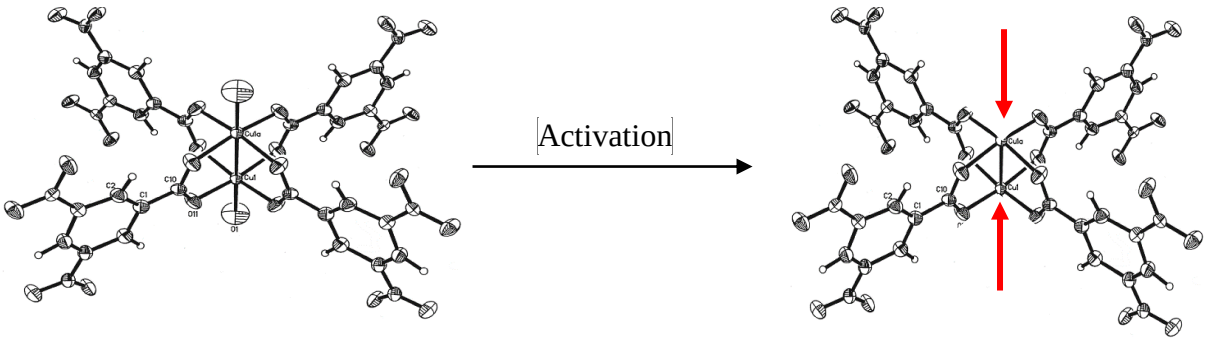


Figure 10: Schematic representation of the activation of HKUST-1

Schlichte *et al.* first reported the catalytic activity of HKUST-1 when they used the HKUST-1 MOF for the trimethylcyanosilation of benzaldehyde [49]. The open framework of this MOF was activated by removing the two water molecules from axial positions in the octahedral framework. The actictivated MOF afforded up to 57% conversion of benzaldehyde reaching a selectivity of 89% at 313K.

Nguyen *et al.* studied the activity of HKUST-1 for the aza-michael reaction in which amines were reacted with α, β-unsaturted carbonyl compounds to prepare β-amino carbonyl compounds and their derivatives. They achieved excellent conversions up to 100% under relatively mild conditions in the presence of 5 mol% activated catalyst. FT-IR and PXRD analysis revealed that the catalyst could be reused several times without a significant reduction in its catalytic potency. Atomic absorption spectroscopy showed that the reaction was not influenced by homogenous catalysis resulting from the leached active species.[50]

Using the same material, Phan *et al.* was able to react phenols and aryl iodides to form diaryl ethers in an Ullman-type coupling reaction. The heterogeneous reaction leads to high conversions using 5 mol% catalyst in the presence of MeONa as a base. The used catalyst was facilely recovered from the reaction mixture using simple filtration and could be reused without significant degradation[51].

Phan *et al.* also reported the highly efficient catalytic activity of HKUST-1 for the C-arylation of acetylacetone in the presence of aryl iodides to obtain aryl ketones as major products. HKUST-1 was confirmed to be a true heterogeneous catalyst as there was no effect of homogeneous catalysis of active species leaching into the reaction mixture [52].Dang *et al.* studied the catalytic activity of HKUST-1 for the synthesis of proparglyamine via direct oxidative C-C coupling reaction using C-H

functionalization between phenylacetylene and N,N-dimethylaniline to give N-methyl-N-(3-phenylprop-2-ynyl)benzenamine as the principal product[53]. The copper-catalyzed reaction afforded 96% conversion after 180 min at 120˚C in the presence of 5 mol% copper-based catalyst. The used catalyst was recovered from the reaction medium by filtration and reused for the coupling reaction. Similarly, HKUST-1 has been used as catalyst for the direct oxidative amination of sp^2 C–H bonds. The reaction involves the use of N-methylmorpholine oxide (NMO) asoxidizing agent in the presence of primary or secondary amine as coupling pairs with DMF as solvent at 90–100^o C [54].

2.3 Statement of Problems

As a result of the urgent global need to ensure efficient energy utilization in the industries and also to reduce the adverse environmental impact of industrial wastes, more efforts have to be geared towards the development of new catalysts that provide the shortest route to organic conversions. Catalysts like MOFs, which are relatively cheap and environment friendly, can go a long way in directing solvent-free routes for safer industrial processes.Despite the great prospects of MOFs for catalysis on both laboratory and industrial scales, relatively small research has been conducted in this area. This can be largely attributed to the fact that most of the MOF-based research are based on gas storage and carbon capture as a matter of importance. MOF catalysis is a promising research area that should be explored with the main aims of reducing energy consumption, reducing the cost of consumer products and minimizing wastes.

2.4 Specific Objectives

1. To synthesize pure crystals of HKUST-1 and Zn-HKUST-1 MOFs via solvothermal method.
2. To modify the synthesized Zn-HKUST-1MOF using transmetallation (including the metal ions like Co (II), Cu(II), Fe(II).

3. To characterize the MOFs using various techniques.
4. To evaluate their catalytic potency as catalysts for oxidation of toluene, cyclohexane and methylcyclohexane.

CHAPTER 3

RESEARCH METHODOLOY

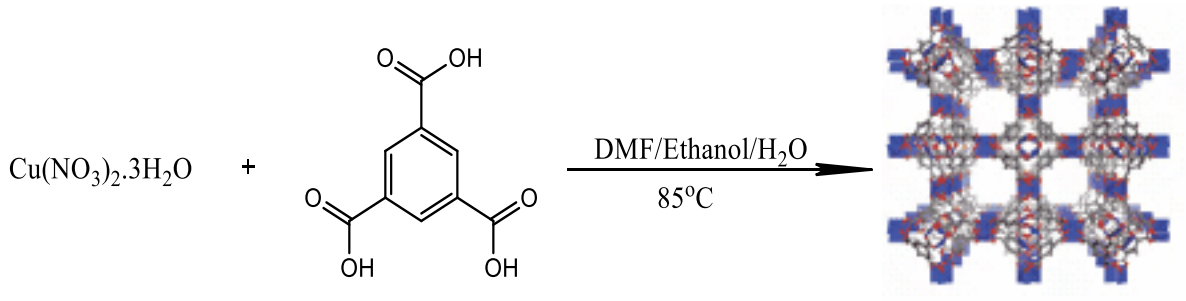
3.1 Materials

All reagents were used as purchased without further purification. 1,3,5-benzene tricarboxylic acid(BTC), $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$,$Zn(NO_3)_2.6H_2O$, $FeCl_2.6H_2O$, N,N-dimethylformamide (DMF) and ethanol were obtained from Sigma-Aldrich. Acetonitrile was obtained from Sigma Aldrich. Toluene, cyclohexane and methylcyclohexane were used as purchased from Sigma-Aldrich. New 10ml and 20ml kimble scintillation vials were used for the synthesis of various MOFs.

3.2 Synthesis of Metal-Organic Frameworks

3.2.1 Synthesis of HKUST-1

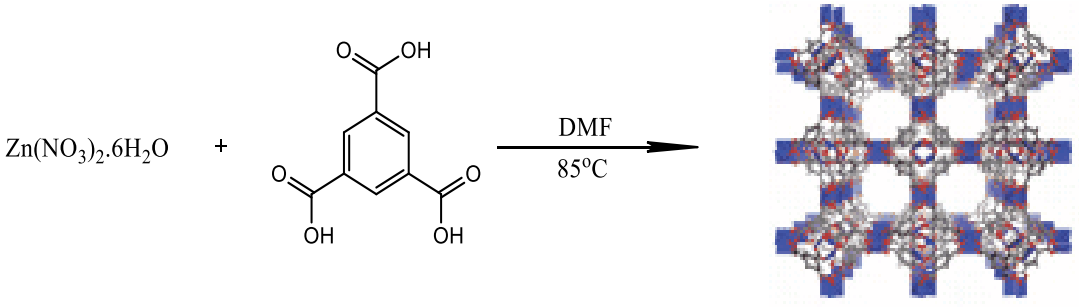
In a typical procedure [55], a mixture of $Cu(NO_3)_2.3H_2O$ (0.438g, 1.81mmol) and 1,3,5-benzenetricarboxylic acid (BTC) (0.236g, 1.12mmol) were completely dissolved in a solvent mixture containing N,N-dimethylformamide (2 ml), deionized water (2 ml) and ethanol (2 ml) in a tightly sealed 20 ml vial. The tightly covered vial was placed in an isothermal oven at 85^oC for 20 hours to yield small, blue, octahedral crystals. After cooling the vial to room temperature, the mother liquor was decanted and the tiny crystals were rinsed with DMF three times. The crystals were then activated by soaking in 5 ml DCM for 3 days at room temperature during which DCM was decanted and freshly replenished three times. The crystals were dried under vacuum at 160^oC for 4 hrs yielding 0.3 g of HKUST-1 in the form of deep blue crystals.



Scheme 1: Typical representation for the synthesis of HKUST-1

3.2.2 Synthesis of Zn-HKUST-1

Using a modified procedure [56], an homogeneous mixture of $Zn(NO_3)_2.6H_2O$ (0.04g, 0.188mmol) and 1,3,5-benzenetricarboxylic acid (BTC) (0.171g,1.12mmol) was dissolved in 10ml N,N-dimethylformamide in a tightly sealed 20ml scintillation vial (**Scheme 2**). The tightly covered vial was placed in an isothermal oven at 85°C for 16 hours to form colorless cubic crystals. After cooling the vial to room temperature, the mother liquor was decanted and the tiny crystals were rinsed with DMF three times. The crystals were then activated by soaking in methanol for 3 days at room temperature during which methanol was decanted and freshly replenished three times. The crystals were dried under vacuum at 170°C for 4 hrs.



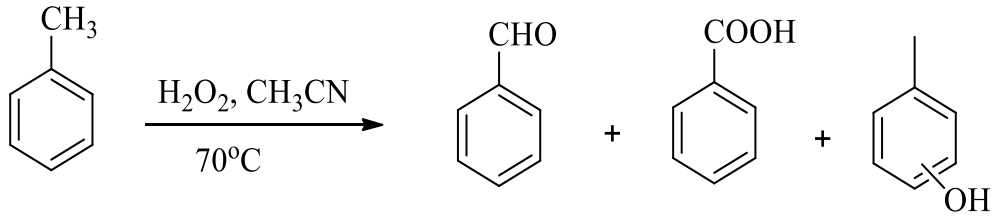
Scheme 2: General procedure for the synthesis of Zn-HKUST-1

3.2.3 Transmetallation of Zn-HKUST-1

Portions of as-synthesized Zn-HKUST-1 crystals were soaked in 0.5M methanolic solutions $Cu(NO_3)_2.3H_2O$, $Co(NO_3)_2.6H_2O$ and $FeCl_2.6H_2O$ for 72 hours at 40^oC. At the end of incubation, solution of metal ions were decanted, and the transmetallated crystals harvested by filtration. The crystals were washed thoroughly with methanol and then soaked in methanol for complete removal of residual metal ions. The resulting cation-exchanged MOFs were dried under reduced pressure at room temperature.

3.2.4 Oxidation of Toluene

The catalytic oxidation of toluene in the presence of hydrogen peroxide as an oxidizing agentwas performed at 70^oC using a 10-point electrothermal reactor (**Figure 11**). 2ml of toluene and 0.03g of an activated catalystwere added into the reaction tube followed by the addition of 4mL of acetonitrile and 2mL of H_2O_2(**Scheme 3**). The reaction mixture was stirred and aliquot of the samples were collected after 6, 12, 18 and 24hours for GC-MS and GC-FID analysis.



Scheme 3: Chemical equation for the oxidation of Toluene

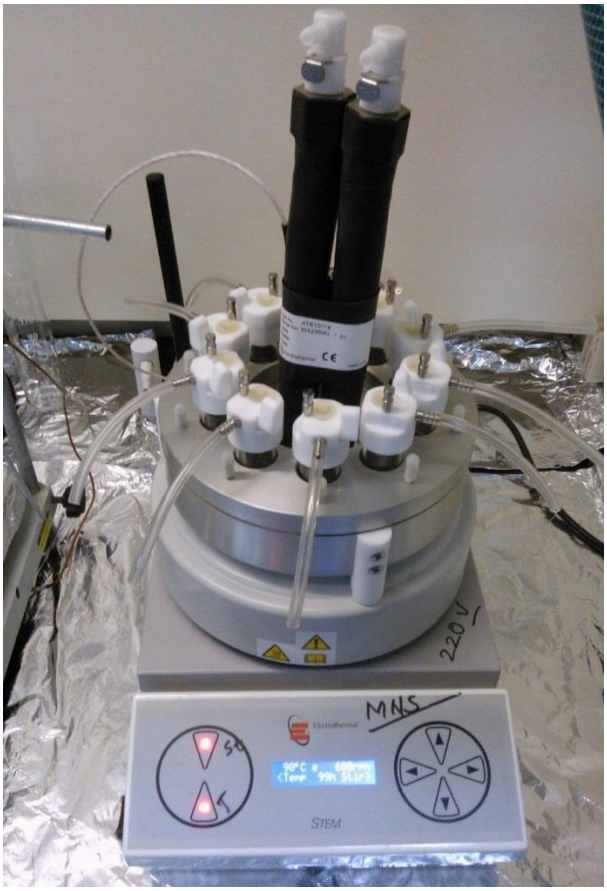
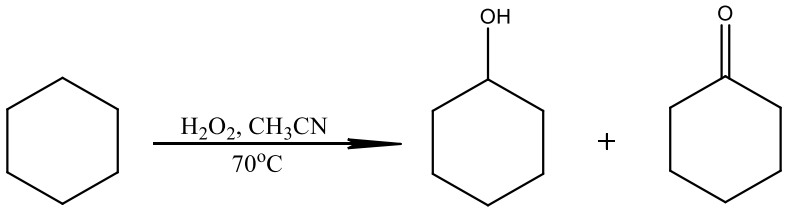


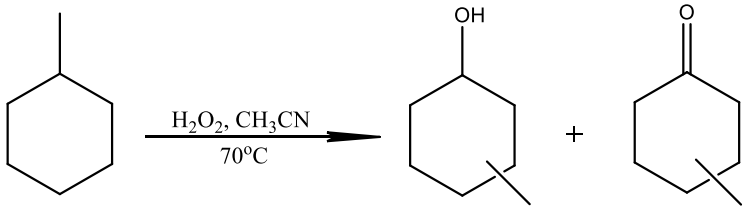
Figure 11: A 10-point electrothermal parallel reactor

3.2.5 Oxidation of Cycloalkanes

The 10-point electro thermal stirrer was charged with a mixture containing the activated catalyst (0.03 g), acetonitrile (4mL), cyclohexane or methylcyclohexane (0.5mL), and 2mL of 30% H_2O_2. The mixture was vigorously stirred and heated 70°C. Aliquots of the reaction mixtures were taken after 6, 12, 18 and 24 hours for GC-MS and GC-FID analysis (**Schemes 4 and 5**).



Scheme 4: Chemical equation for the oxidation of cyclohexane



Scheme 5: Chemical equation for the oxidation of methylcyclohexane

CHAPTER 4

RESULTS AND DISCUSSION

Pure samples of HKUST-1 and Zn-HKUST-1 MOFs were obtained as blue and colorless crystals, respectively.The crystals were dried under vacuum at 120°C and stored in air-tight vial to prevent

moisture. The dried samples were characterized using Fourier transform Infrared Spectrophotometry (FT-IR), Scanning Electron Microscopy (SEM) and Powder X-ray Diffraction (PXRD).

4.1 FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

FTIR spectra were taken on a Nicolet spectrophotometer using KBr within the standard range of 4000-400cm^{-1}. This method was used to confirm the formation of HKUST-1, Zn-HKUST-1 as well as transmetallated Zn-HKUST-1 isostructural MOFs as shown (Figures 12-17). 1,3,5-benzenetricarboxylic acid(BTC) as a ligand shows the C=O stretching frequency of carboxylic acid around 1718cm^{-1} and also a broad O-H peak at about 2933cm^{-1}which corresponds to the hydrogen bonding (**Figure 12**). The FT-IR of HKUST-1 and Zn-HKUST-1 indicates that there was a significant shift in the C=O stretching frequency of the BTC ligand. The disappearance of the broad acidic OH peak of BTC at 2933$cm^{-1}$was the result of deprotonation that leads to coordination. The band for the O-C-O asymmetric stretching of HKUST-1 and Zn-HKUST-1 appeared at 1658cm^{-1} and 1640cm^{-1} respectively, due to the binding of the carbonyl oxygen with metal atoms (**Figures 13 and 14**). The sharp peaks at 3433$cm^{-1}$for Zn-HKUST-1 (**Figure 13**) and 3434cm^{-1} (**Figure 14**) are due to the axial H_2O ligands that are coordinated to the dimeric Cu atoms forming an octahedral unit.

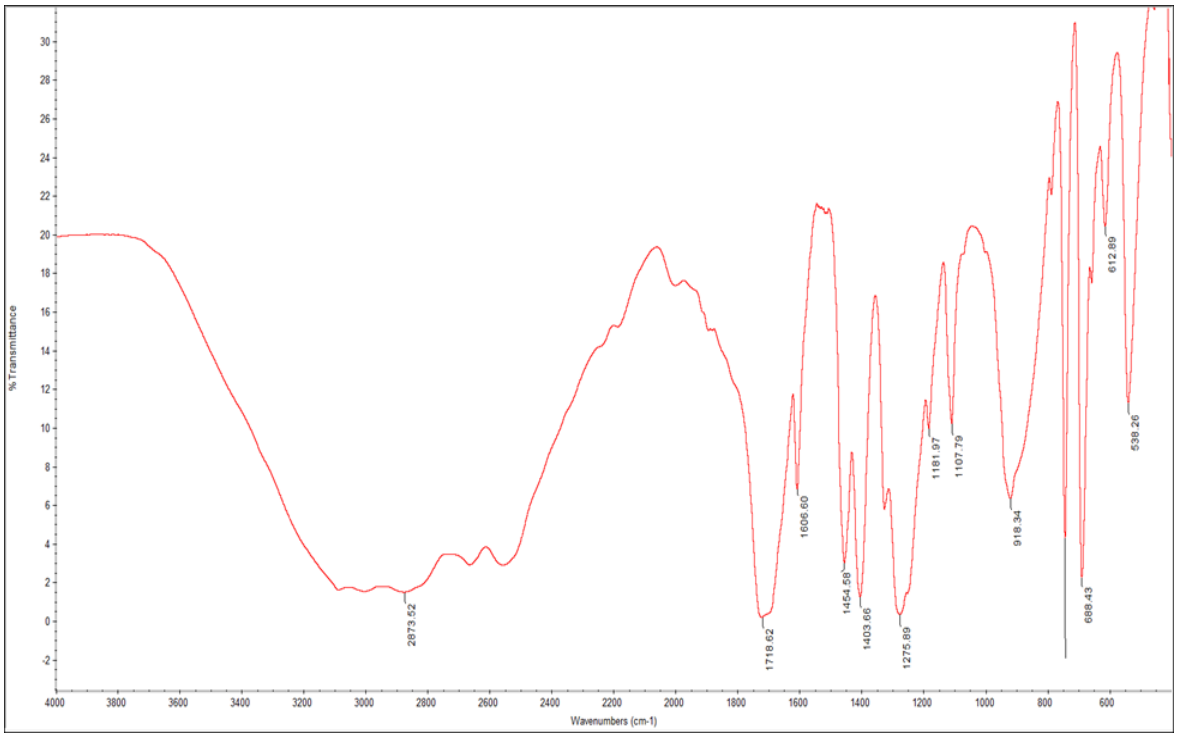


Figure 12: FT-IR spectrum of 1,3,5-benzenetricarboxylic acid (BTC)

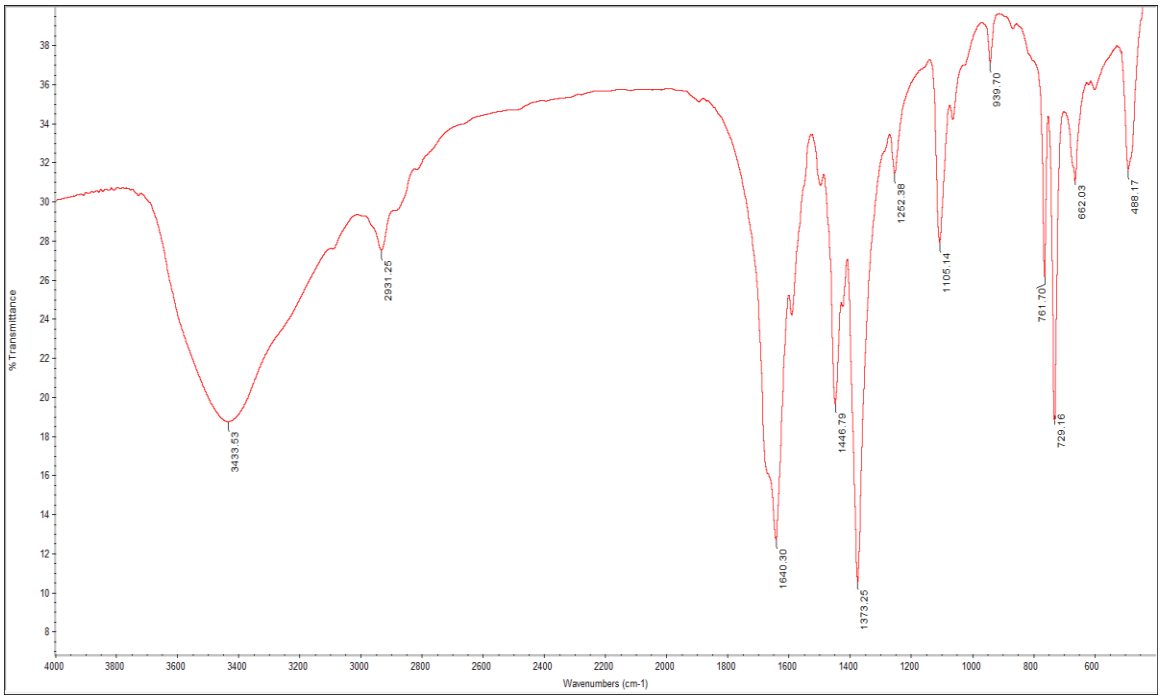


Figure 13: FT-IR Spectrum for HKUST-1

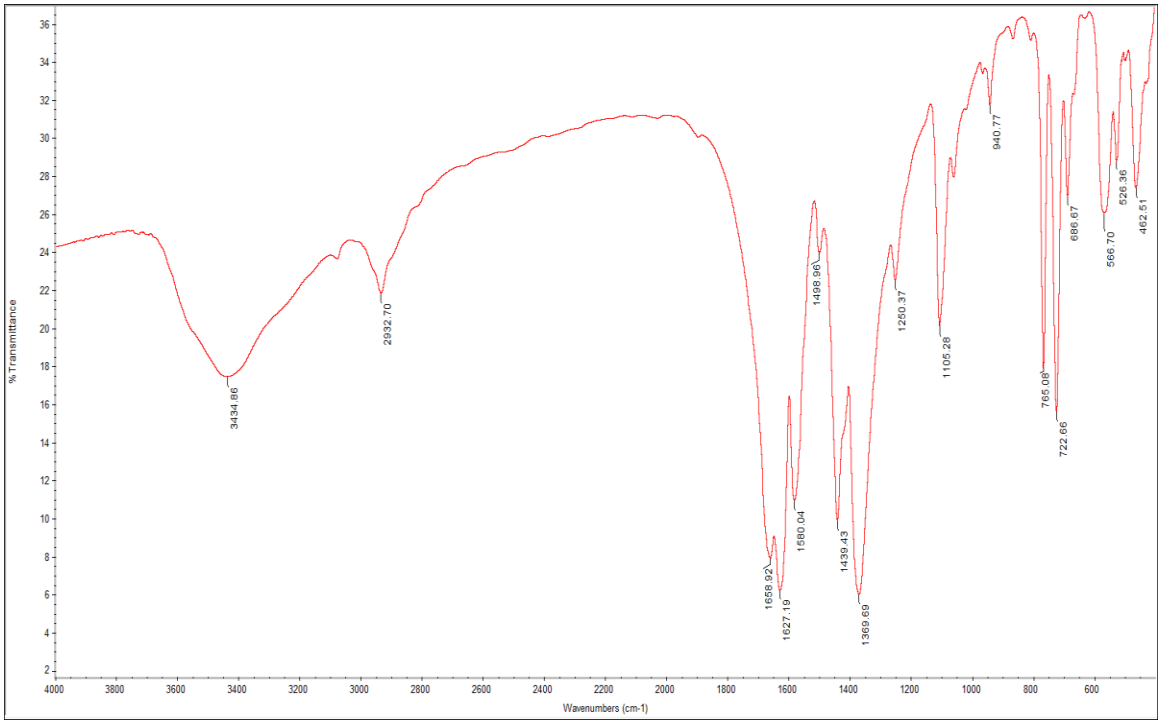


Figure 14: FT-IR Spectrum for Zn-HKUST-1

Similarly, FT-IR spectra of Fe-Zn-HKUST-1, Co-Zn-HKUST-1 and Cu-Zn-HKUST-1 (**Fig. 15-17**) show great similarity to that of Zn-HKUST which indicates that there retention of the MOF framework after transmetallation.

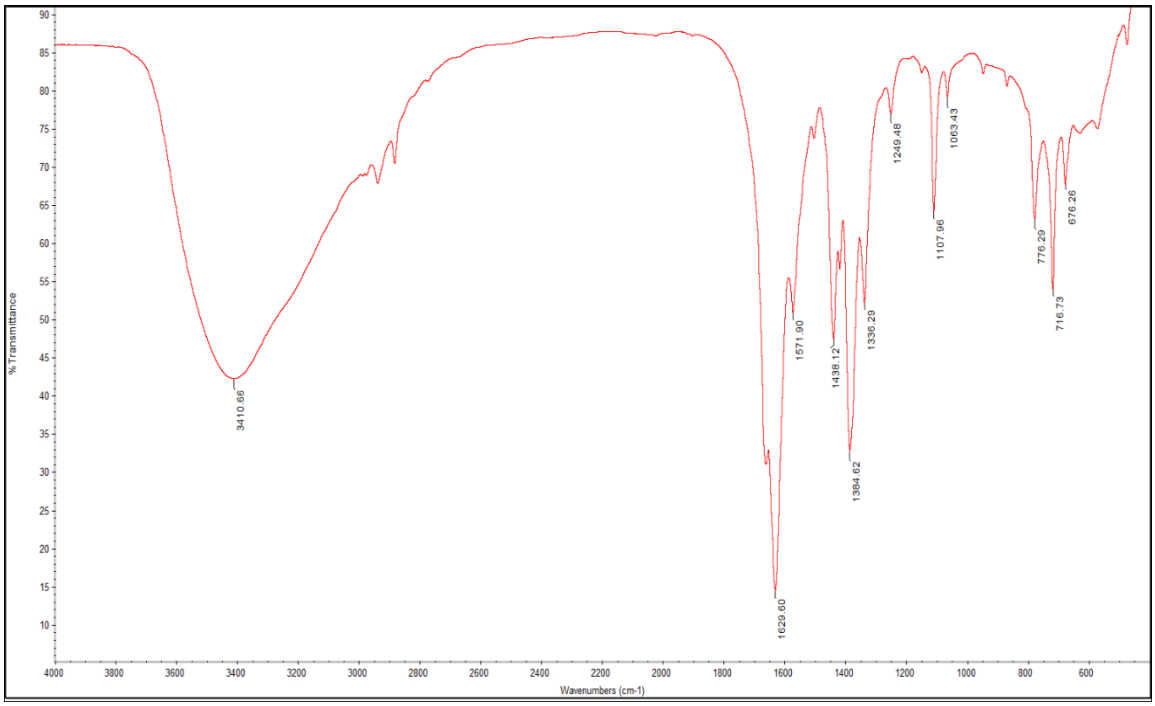


Figure 15: FT-IR Spectrum for Fe-Zn-HKUST-1

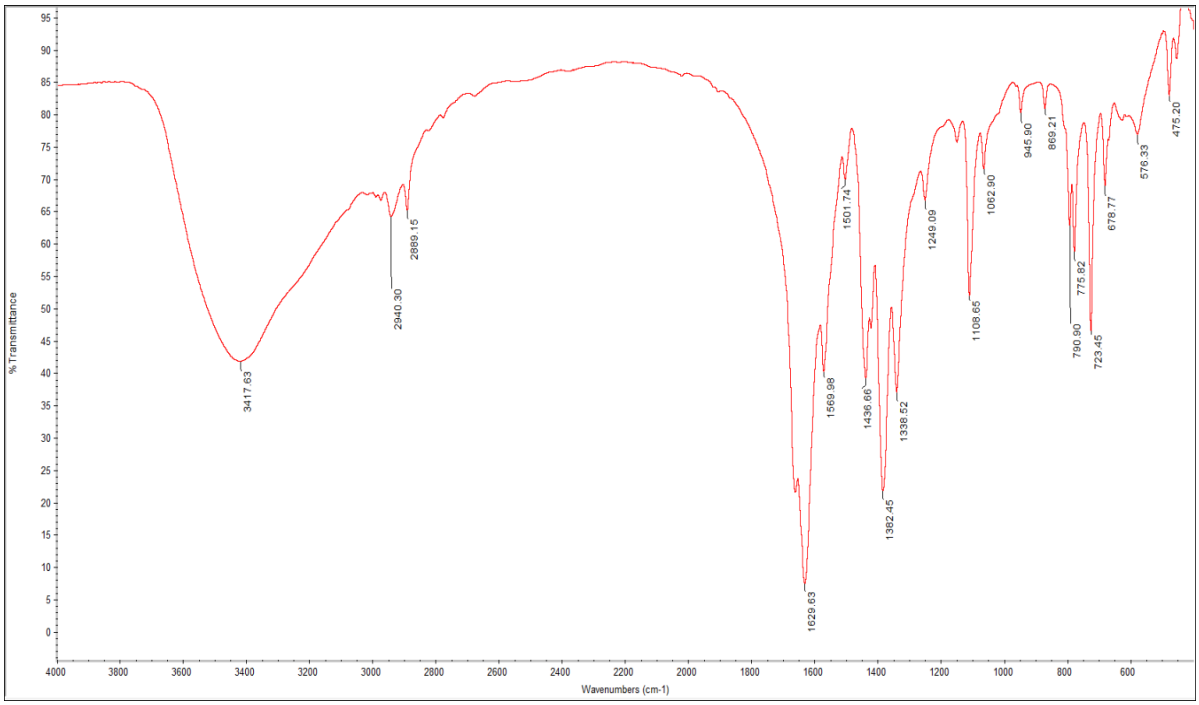


Figure 16: FT-IR Spectrum for Co-Zn-HKUST-1

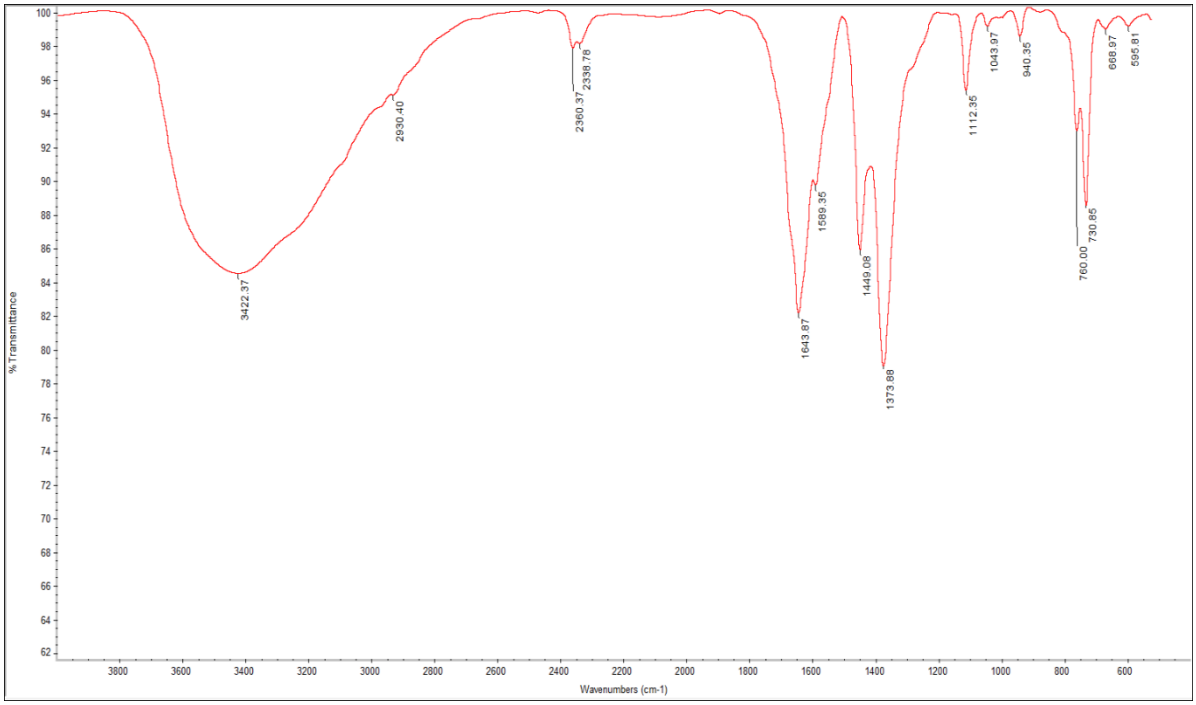


Figure 17: FT-IR Spectrum for Cu-Zn-HKUST-1

4.2 FIELD EMISSION SCANNNG ELECTRON MICROSCOPY (FESEM)

Field emission scanning electron microscope (FESEM, Tescan-Lyra-3) was used to provide images of the synthesized catalysts. Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signal at the surface of solid specimens. The signals that are derived from electron – sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Accelerated electrons in a SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron – sample interaction when the incident electrons are decelerated in the solid samples. These signals include **secondary electrons** (that produce SEM images), **backscattered electrons** (BSE), **diffracted backscatteredelectrons** (EBSD) that are used to determine crystal structures and orientations. Secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase sample (i.e. for rapid phase discrimination). **Figures 18 and 19** show the SEM images of the synthesized catalysts with the same magnification of 2μm-20μm scale bar. The micrographs show the formation of crystalline materials as expected. HKUST-1 occurred was observed to be a polyhedral(octahedral) crystal **(Figure 18)** with sizes of few microns. The micrograph of Zn-HKUST-1 shows the formation of a polyhedral (Cubic) crystals with sizes in few microns **(Figure 19).**

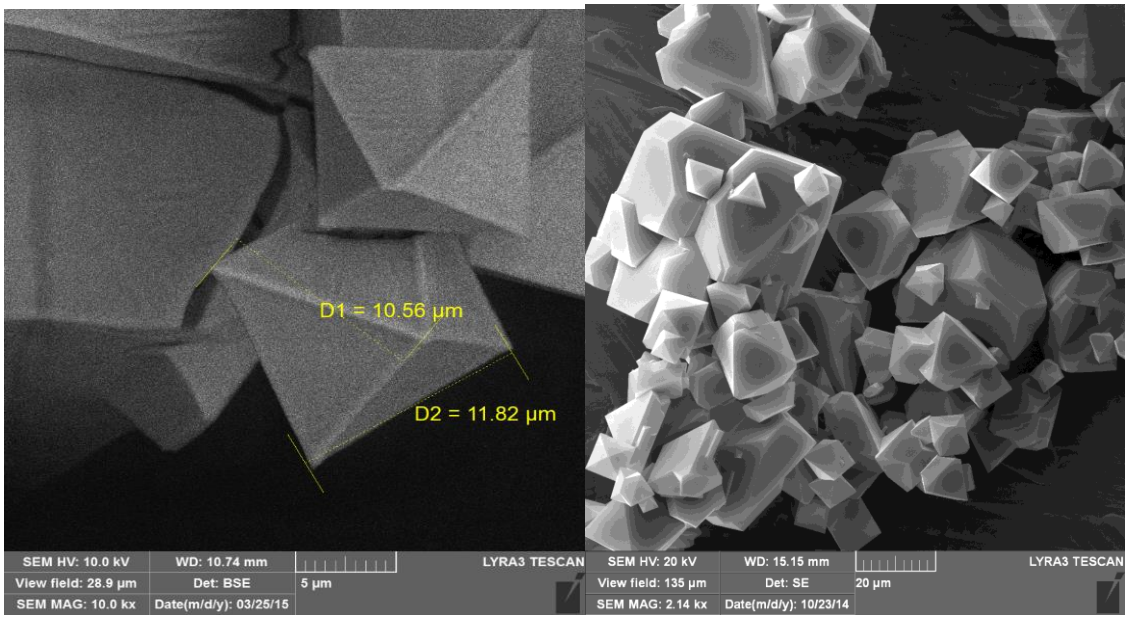


Figure 18: SEM Micrographs for HKUST-1

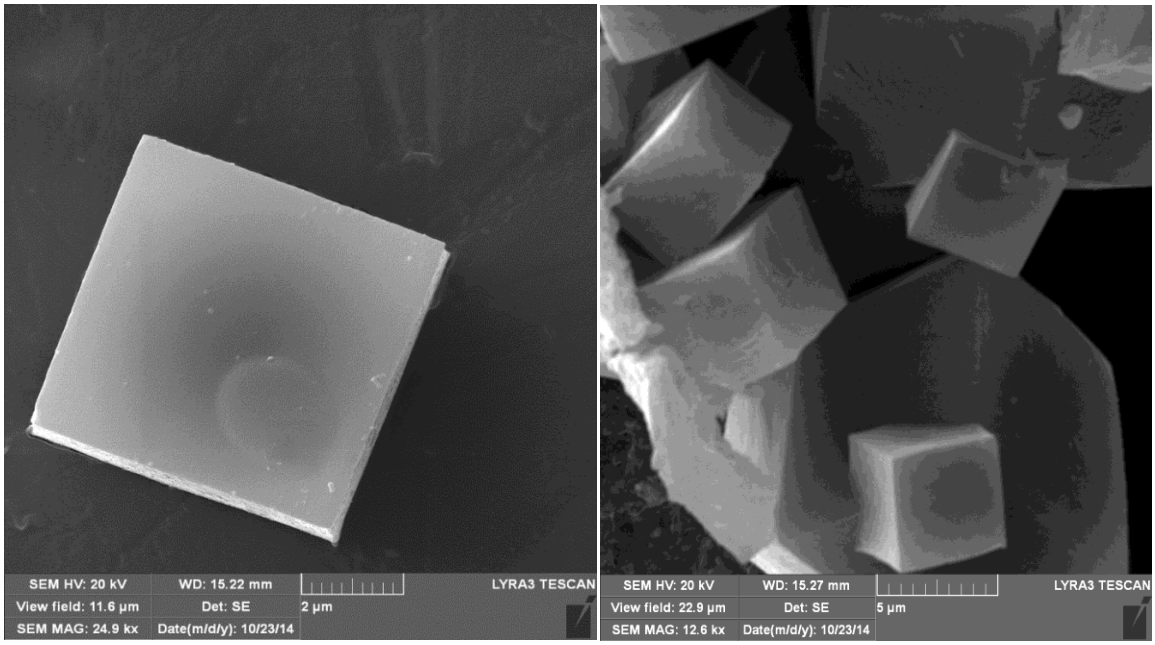


Figure 19: SEM Micrograph for Zn-HKUST-1

4.3 POWDER X-RAY DIFFRACTION (P-XRD)

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex II instrument with a monochromator of CuKα1 (1.5406Å) at 30kV, 15mA. The PXRD patterns were recorded in the static scanning mode from 5^o to 60^o (2Θ) at a detector angular speed of $2^o\Theta min^{-1}$ and step size of 0.02^o. The wavelength of X-rays is approximately the same as distance between the particles in the lattice. If the beam of X-rays strikes a crystal, the X-rays are deflected by the crystal and are detected by a photographic plate. This technique was used to examine the morphological structure of the synthesized catalyst. The crystallinity of HKUST-1 and Zn-HKUST-1 was probed by PXRD after solvent evacuation under reduced pressure at elevated temperatures. The diffraction patterns show that HKSUT-1 **(Figure 18)** appears isostructural to Zn-HKUST-1 **(Figure 19)**, with a slightly larger unit cell (HKUST-1, a = 26.343(0.005 Å) Zn-HKUST-1, a = 26.520(0.001 Å). The respective patterns were compared to those found in the Cambridge Structural Database (CSD). The CSD reference patterns were simulated using Mercury V. 3.3 software. Differences in peak intensities between simulated and experimental diffractograms can be attributed to pore occlusion by coordinated guest molecules.

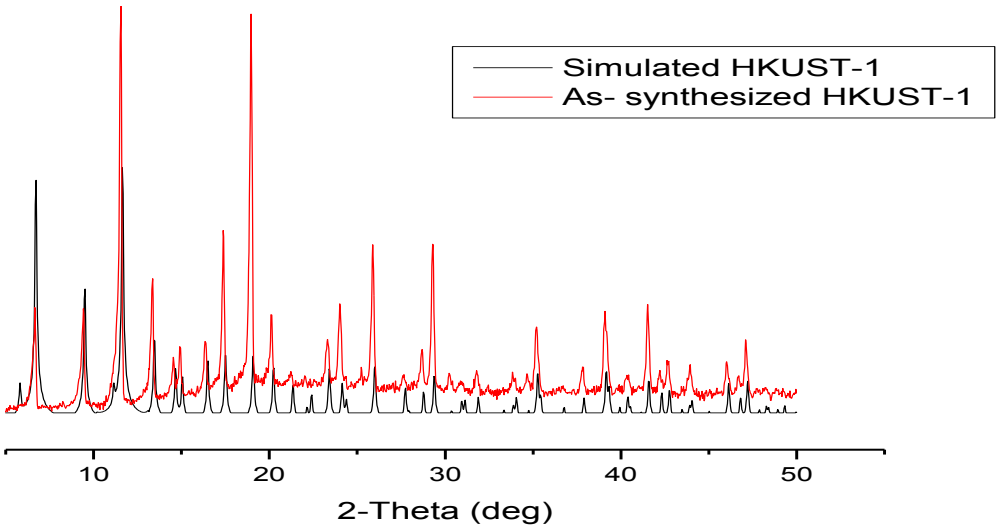


Figure 20: Simulated and experimental Powder XRD Patterns for HKUST-1

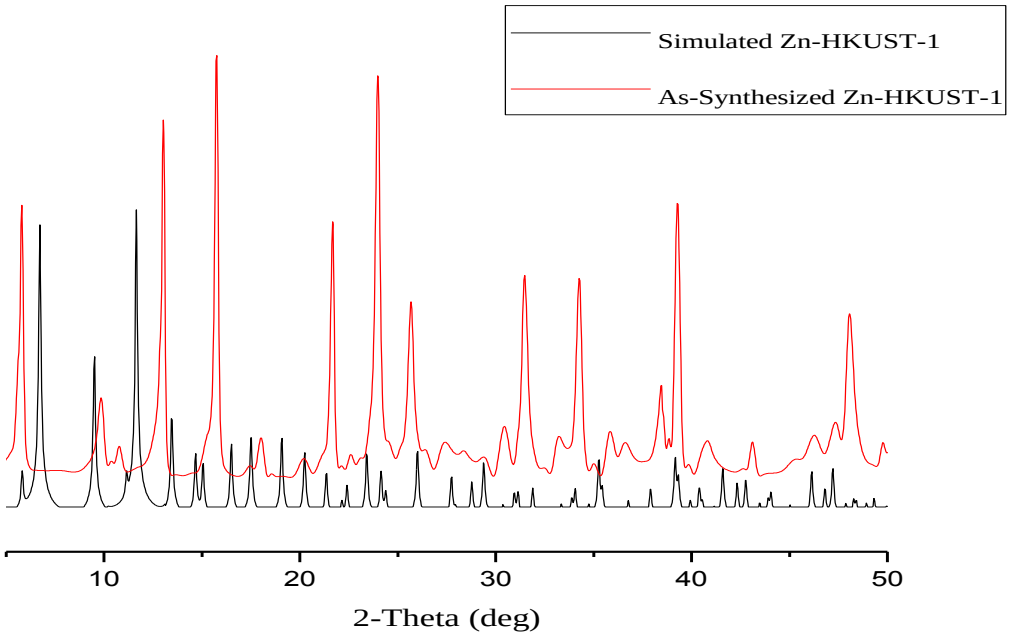


Figure 21: Simulated and experimental Powder XRD patterns for Zn-HKUST-1

The powder patterns of Fe-Zn-HKUST-1, Co-Zn-HKUST-1 and Cu-Zn-HKUST-1 show that the modified MOFs are isostructural to Zn-HKUST-1. This can be confirmed since the XRD pattern of each of the modified MOF shows a reasonable level of similarity to the confirmed Zn-HKUST-1 pattern.

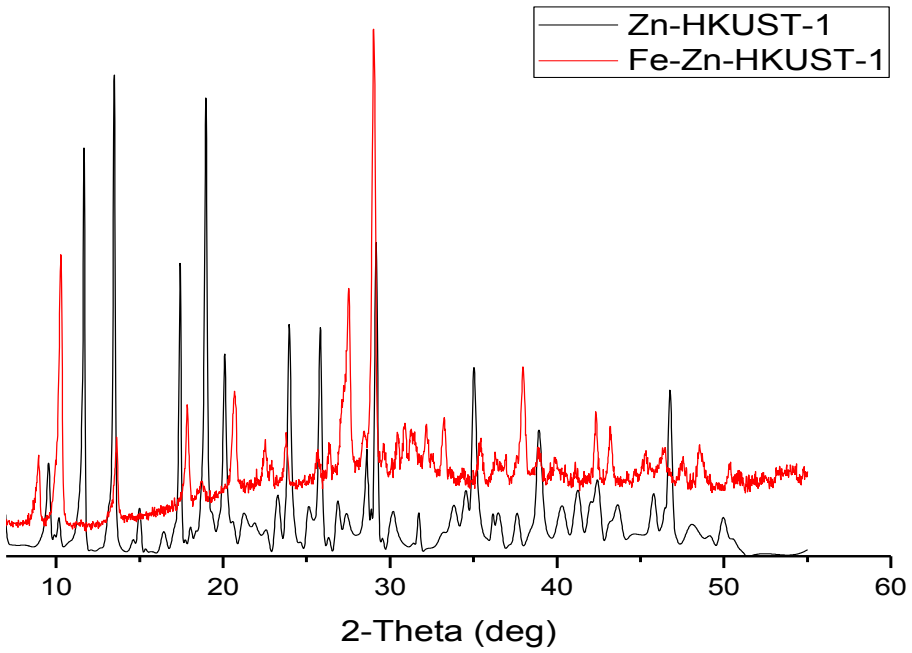


Figure 22: Comparative Powder pattern for Zn-HKUST-1 and Fe-Zn-HKUST-1

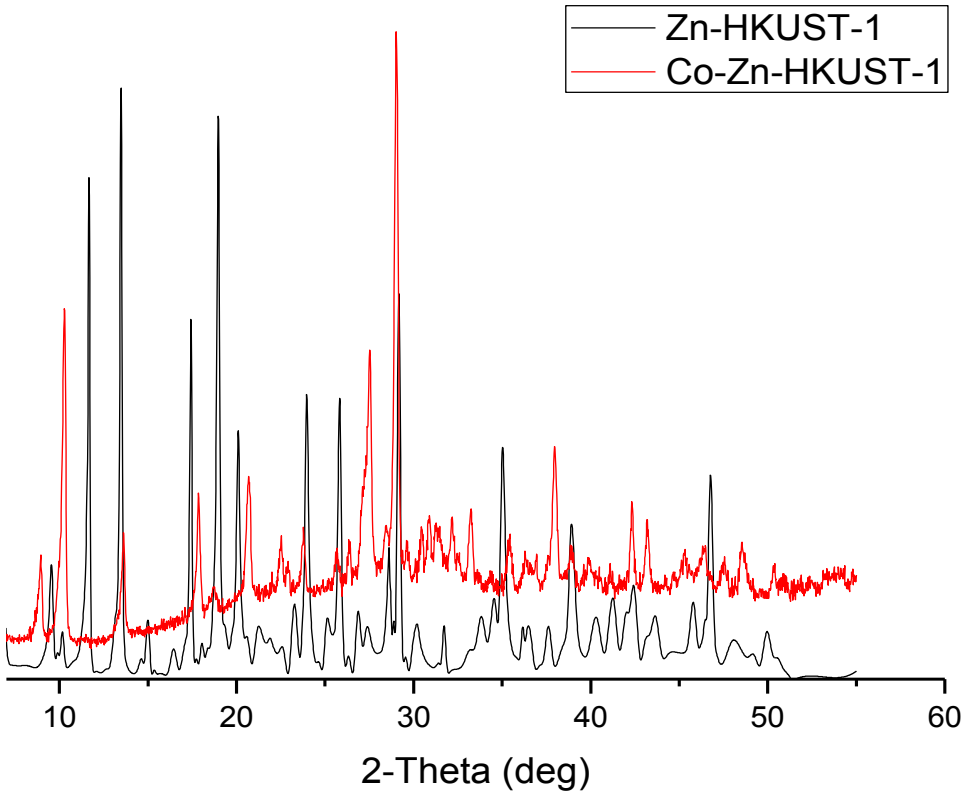


Figure 23: Comparative Powder XRD Patterns for Zn-HKUST-1 and Co-Zn-HKUST-1

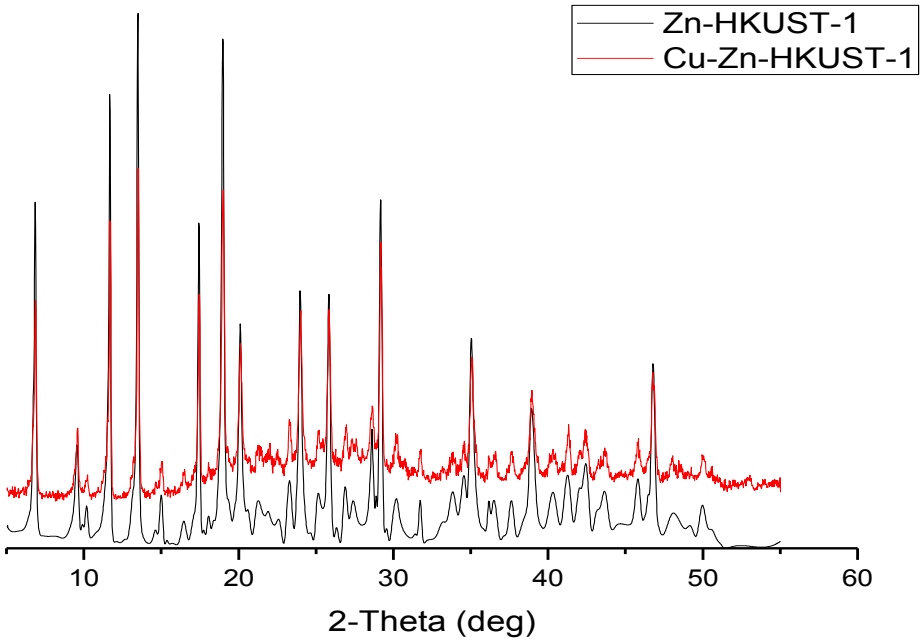


Figure 24: Comparative Powder XRD Patterns for Zn-HKUST-1 and Cu-Zn-HKUST-1

1.4 INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS)

It is an analytical technique which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{15} (part per quadrillion, ppq). The working principle is based on the ionization of the sample with an inductively coupled plasma followed by the accurate separation and quantification of those ions with mass spectrometer. Compared to atomic absorption spectroscopy, ICP-MS has better sensitivity, precision and speed. Prior to ICP-MS analysis, the Fe-Zn-HKUST-1, Co-Zn-HKUST-1 and Cu-Zn-HKUST-1 were digested using 30% HNO_3 solution and the samples were further diluted to 10ppm.

The ICP-MS analysis of Fe-Zn-HKUST-1 revealed that 34% of the Zn^{2+} in Zn-HKUST-1 was replaced by Fe^{2+}indicating that the transmetallation was incomplete. Similarly, 34% of the Zn^{2+} in Zn-HKUST-1 was replaced by Co^{2+}ions. On the other hand, the analysis of metal ions in Cu-Zn-HKUST-1 showed that 90% of the Zn^{2+} ions were replaced by Cu^{2+}.

1.5 CATALYTIC ACTIVITY

1.5.1 Oxidation of Toluene

The oxidation of toluene proceeded in the presence of H_2O_2as an oxidizing agent using acetonitrile as a solvent to give a mixture of oxygenated products as expected. The formation of a mixture of products was the first test of the catalytic activity of the MOFs. The blank experiment in the absence of the MOF did not lead to significant toluene conversion even after 24 hours. The outcome of the blank experiment was similar to what has already been reported [57]. HKUST-1 showed good activity for the title reaction affording a conversion of 51% after 6 hours**(Table 1)**.

Cresols were the major products and their amounts in the product mixture decreased from 65% after 6 hours to 58% after 24 hours due to the formation of benzoic acid as by-product. The formation of cresols in this reaction is not surprising as this could be as a result of the hydroxylation of the aromatic ring in the presence of peroxide. The selectivity in benzaldehyde was also significantly decreasing from 18% in 6 hours to 16% after 24 hours as the selectivity of benzoic acid has increased with time. This suggests that the rate of benzoic acid formation from benzaldehyde is faster than the rate of toluene oxidation.

Table 1: Toluene Oxidation with HKUST-1

Time(hr)	**% Conversion**	**Benzaldehyde (%)**	**Benzoic acid (%)**	**Benzyl Alcohol (%)**	**O, m, p - Cresols(%)**
6	51	18	17	trace	65
12	60	19	20	trace	61
18	77	17	25	trace	58
24	80	16	26	trace	58

Despite the fact that Zn is not a good oxidation metal, Zn-HKUST-1 pushed the oxidation of toluene to 22% after 24 hours with 22% selectivity **(Table 2).**This could be attributed to the electronic structure of the MOF resulting from the coordination of the BTC ligand. The effect of time can also be easily observed by considering the significant differences in conversion and benzaldehyde selectivity with the progress of the reaction. It should be noted that the Zn-HKUST-1 catalyst did not favor further oxidation of benzaldehyde to benzoic acid.

The incorporation of Fe into the Zn-HKUST-1 framework gave a significant improvement to the catalytic activity as shown in T**able 3.** Apart from the gradual initial increase in the conversion that can be attributedto the presence of Fe, Fe-Zn-HKUST-1, clearly exemplified the unique performance of Fe in oxidation reactions, especially in terms of selectivity giving the highest benzaldehyde selectivity of 61% at 6 hours.

Table 2: Toluene Oxidation using Zn-HKUST-1

Time(Hr)	% Conversion	Benzaldehyde (%)	Benzoic acid (%)	O, m, p – Cresols(%)
6	1.7	0	0	100
12	10	8	0	92
18	19	18	0	82
24	22	22	0	78

Table 3: Toluene Oxidation using Fe-Zn-HKUST-1.

Time(hr)	% Conversion	Benzaldehyde (%)	Benzoic acid (%)	O, m, p - Cresols(%)
6	17	61	6	33
12	20	60	6	34
18	28	60	7	33
24	30	57	8	35

Unlike Fe-Zn-HKUST-1, Co-Zn-HKUST-1 gave similar performance to Zn-HKUST-1 **(Table 4)**.

Table 4: Toluene Oxidation withCo-Zn-HKUST-1

Time(hr)	% Conversion	Benzaldehyde (%)	Benzoic acid (%)	O, m, p - Cresols(%)
6	1	16	0	84
12	16	25	0	75
18	20	28	0	72
24	38	32	0	68

Table 5: Toluene Oxidation with Cu-Zn-HKUST-1

Time(Hr)	% Conversion	Benzaldehyde (%)	Benzoic acid (%)	O, m, p - Cresols(%)
6	34	16	13	71
12	56	14	14	72
18	65	17	17	66
24	70	18	15	67

Table 5 shows the catalytic activity of Cu modified Zn-HKUST-1 for toluene oxidation and it is evident that Cu has greatly improved the conversion of toluene relative to Zn-HKUST-1. After 6 hours Cu-HKUST-1 gave a conversion of 34% with 16% benzaldehyde selectivity, while Zn-HKUST on the other hand gave very low conversion without benzaldehyde at the same time.

4.5.2 Oxidation of Cyclohexane

The isostructural HKUST-1 metal-organic frameworks acted as catalysts for the oxidation of cyclohexane with H_2O_2 at 70^oC forming cyclohexanol and cyclohexanone as major products (**tables 5-10**). HKUST-1 was observed to be the most active catalyst, achieving the highest conversion of 52% which is better than those of well-known catalytic materials [61, 62] and comparable to that of modified zeolite [63]. The catalyst gave an initial low conversion of 9% but this value increased steadily as the reaction progresses to 24 hours. Thegreat activity of HKUST-1 could be largely attributed to the heavy presence of vacant Cu sites in the framework. On the other hand, Zn-HKUST-1 did not show any significant activity for this reaction even after 24 hours. This inactivity of Zn-HKUST-1 could be due to the d^{10} electronic configuration of the Zn-metal which is unfavorable for alkane oxidation.

Table 6: Oxidation of Cyclohexane using HKUST-1

Time(Hr)	**% Conversion**	**Cyclohexanone**	**Cyclohexanol**
		%	**%**
6	9	100	-
12	29	77	23
18	39	60	40
24	52	60	40

Drastic improvement in activity was observed when Fe was incorporated into the framework of Zn-HKUST-1**(table 7).** Fe-HKUST-1 gave the highest conversion of 15% after 24 hours. Similarly, Co-Zn-HKUST-1 afforded 14% conversion with reasonable selectivity in cyclohexanol and cyclohexanone as shown in **table 8**.

Table 7: Oxidation of Cyclohexane using Fe-Zn-HKUST-1

Time (Hr)	**% Conversion**	**Cyclohexanone %**	**Cyclohexanol %**	**4-hydroxy Cyclohexanone(%)**	**1,4-cyclo hexadione (%)**
6	5	45	28	25	2
12	7	59	26	12	3
18	13	56	21	18	5
24	20	55	20	21	4

Table 8: Oxidation of Cyclohexane usingCo-Zn-HKUST-1

Time(Hr)	**% Conversion**	**Cyclohexa none (%)**	**Cyclohexanol (%)**
6	2	55	25
12	9	60	40
18	15	65	35
24	27	65	35

Table 9 shows the result of cyclohexane oxidation in the presence of Cu-Zn-HKUST-1. It gave a conversion of 40% after 24 hours with equal ratio of cyclohexanonl and cyclohexanone. The activity

of Cu-Zn-HKUST-1 is similar to what was observed for HKUST-1 in terms of the conversion and this could be attributedto the Cu atoms which are probably responsible for the relatively high conversions.

Table 9: Oxidation of Cyclohexane using Cu-Zn-HKUST-1

Time (Hr)	% Conversion	Cyclohexanone (%)	Cyclohexanol (%)
6	7	69	31
12	15	56	44
18	33	55	45
24	40	51	49

1.5.2 Oxidation of Methylcyclohexane

Methylcyclohexane was oxidized using the isostructural MOFs at 70^{o}C in the presence of H_2O_2 to afford reasonable yields of oxygenated products. GC-MS analysis revealed the formation of 5 different oxygenated products methylcyclohexanol and methylcyclohexanone being the major products. HKUST-1 gave the highest conversion of 48% for this reaction after 24 hours with methylcyclohexanol as the major product while it afforded only 18% conversion after 6 hours (**Table 10**). The difference in reaction time largely affects the conversion but has little effect on the methylcyclohexanol selectivity.

Table 10: Oxidation of Methylcyclohexane using HKUST-1

Time(Hr)	% Conversion	Methylcyclohexanol (%)	Methyl cyclohexanone (%)	Cyclohexane methanol (%)	Cyclohexanal (%)
6	18	56	27	17	trace
12	31	64	11	25	trace
18	35	59	16	20	05
24	48	58	19	18	05

The modification of Zn-HKUST-1 however generally improved its activity for methylcyclohexane oxidation. Table 11 shows the result of methylcyclohexane oxidation in the presence of Fe-Zn-HKUST-1. 3% conversion of the substrate was observed in 6 hours with equal amounts of methylcyclohexanol and methylcyclohexanone. There was a gradual increase in the percent conversion to 15% after 24 hours. It is easy to note the effect of Fe incorporation into the Zn-HKUST-1 framework since only Zn-HKUST-1 was not active up to 24 hours under the same reaction conditions.

Table 11: Oxidation of methylcyclohexane using Fe-Zn-HKUST-1

Time (Hr)	% Conversion	Methylcyclo-hexanol (%)	Methyl cyclohexanone (%)	Cyclohexane methanol (%)	3-hepten-2-one (%)
6	3	42	51	Trace	7
12	10	53	39	trace	8
18	12	49	35	3	13
24	15	45	37	8	10

Similarly, Co-Zn-HKUST showed appreciable activity over Zn-HKUST-1 due to the presence of Co atoms in the MOF framework (**table 11**). **Table 12** shows the results obtained for the liquid phase oxidation of methylcyclohexanol where the highest conversion of 45% was observed after 24 hours forming higher amount of methylcyclohexanol.

Table 12: Oxidation of Methylcyclohexane using Co-Zn- HKUST-1

Time(Hr)	% Conversion	Methylcyclo hexanol (%)	methyl cyclohexanone (%)	Cyclohexane methanol (%)	3-hepten-2one (%)
6	6	43	57	-	trace

12	7	61	33	-	6
18	10	45	51	-	4
24	14	44	39	4	13

Table 13**: Oxidation of Methylcyclohexane using Cu-Zn-HKUST-1**

Time(Hr)	**% Conversion**	**Methylcyclohexanol (%)**	**Methylcyclohexanone (%)**	**Cyclohexane methanol (%)**	**Cyclohexanal (%)**
6	18	55	27	18	-
12	29	65	15	20	-
18	40	60	16	20	4
24	45	66	14	17	3

1.5.3 REUSABILITY OF THE CATALYSTS

The HKUST-1 metal organic framework was recovered, washed and reactivated for two more runs after 6 hours. The dried HKUST-1 was subjected to powder x-ray diffraction to know if the MOF framework was able to withstand the reaction condition. The PXRD analysis revealed that there was no collapse in the MOF framework after 6 hours since there is great match between the patterns for the unused and used HKUST-1 **(Figure25).** Since the catalyst was found to be structurally intact, the

catalytic activity was tested for toluene oxidation in two repeated runs. There was retention of activity in terms of conversion of toluene and selectivity for benzaldehyde **(Figure 26).**

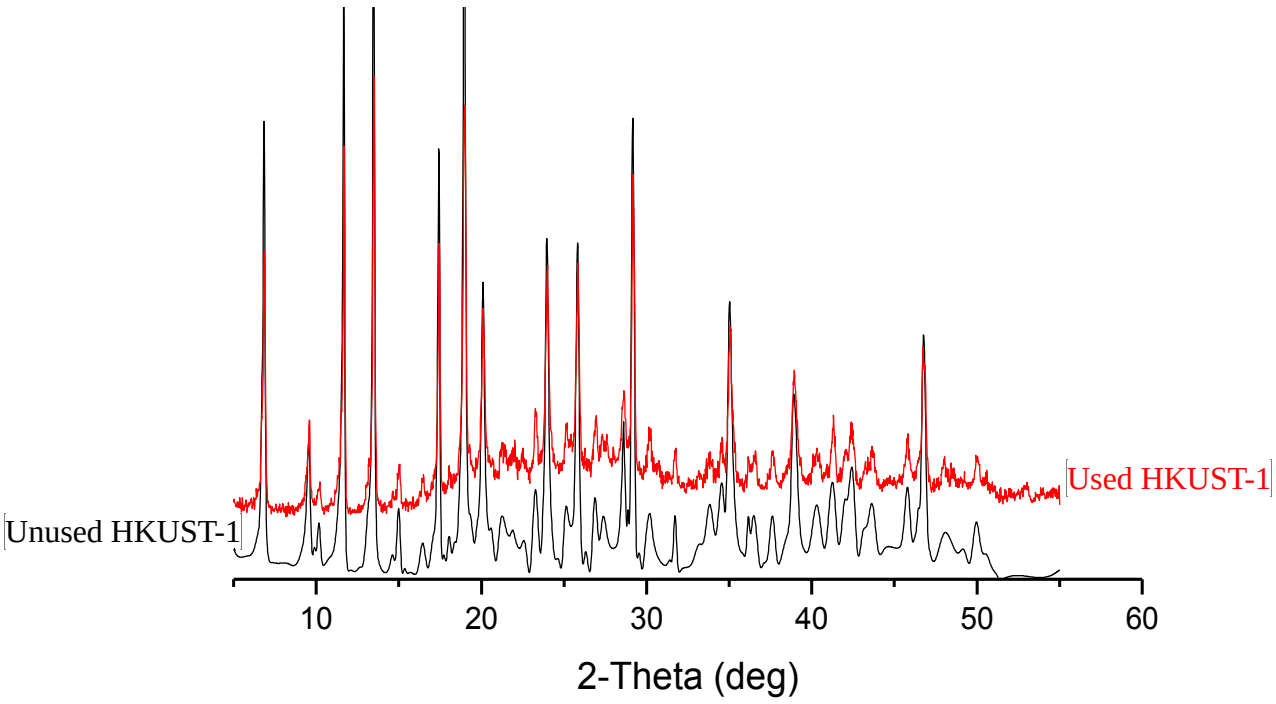


Figure 25: PXRD patterns for used and unused HKUST-1 Metal-Organic Framework

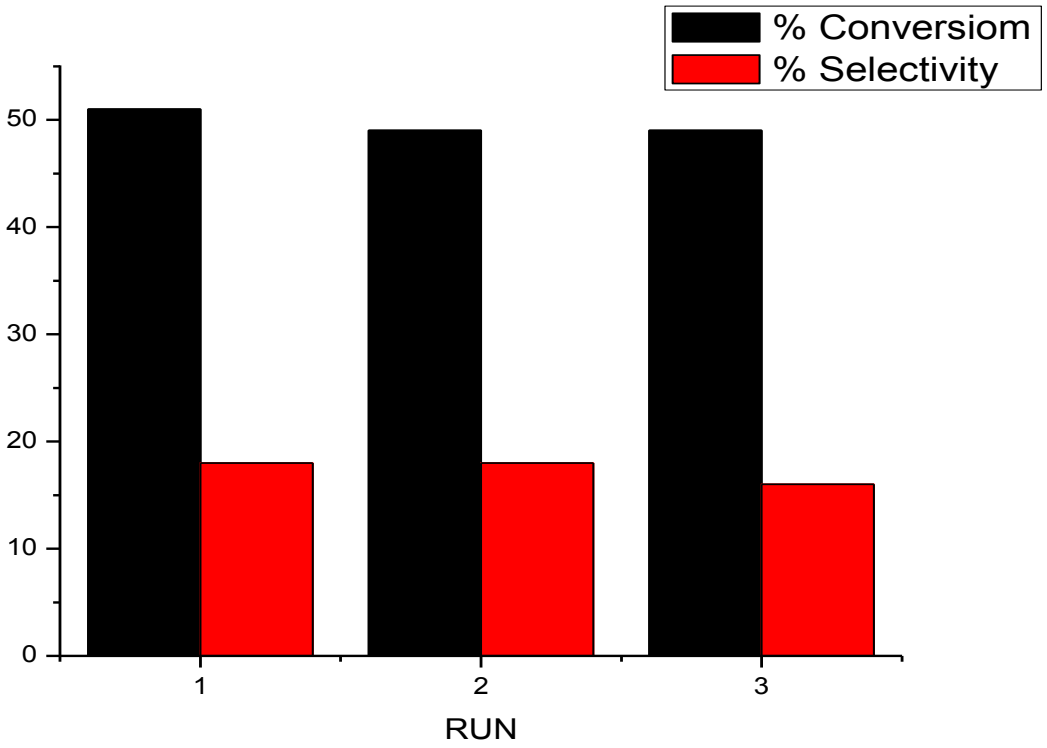


Figure 26: Reusability of HKUST-1 for Toluene Oxidation

CONCLUSION

Pure single crystals of HKUST-1 and Zn-HKUST-1 were successfully synthesized using solvothermal method and the synthesized Zn-HKUST-1 was subjected to modification via transmetallation affording reasonable amounts of the transmetallated products. Both the synthesized and modified MOFs were characterized using FTIR, FESEM, PXRD and ICP-MS. Furthermore, the

catalytic activity of the MOFs was tested in the oxidation of toluene, cyclohexane and methylcyclohexane. Fe-Zn-HKUST-1 gave the best activity in terms of benzaldehyde selectivity for the oxidation of toluene. However, HKUST-1 gave the highest conversion of 52% for cyclohexane and methylcyclohexane oxidation.

RECOMMENDATIONS

1. Metal-organic frameworks containing Fe, Mn and V should be further studied for their potential for oxidation reactions.
2. Air oxidation should be considered for better benzaldehyde selectivity during toluene oxidation.
3. HKUST-1 nanocomposites should be tested for more oxidation reactions.
4. Transmetallated Zn-HKUST-1 MOFs should be tested for their gas storage and chemical sensing properties.
5. Further studies should be conducted to determine exactly how porosity and surface area affect the catalytic activity of MOFs.

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